Thermochemistry, Structure and Reactivity of the Trifluoromethoxy Radical

J. S. Francisco and J. I. Steinfeld
Massachusetts Institute of Technology, Cambridge, Mass. 02139, U.S.A

I. H. Williams
University of Cambridge, U.K.

The importance of halomethanes in the chemistry of the atmosphere relates to their possible threat to the stratospheric ozone layer via photodissociation to X$^{\bullet}$ and $CX_3^{\bullet}$ (where X = F and Cl) radicals, but relatively little is known regarding the fate of the latter fragment. In order to investigate the role of CX_3 radicals in the chemistry of the atmosphere, thermochemical estimates [1] have been made for reactive intermediates which may be involved in the oxidation of $CX_3^{\bullet}$. In this study we consider the fate of the simplest trihalomethyl fragment, $CF_3^{\bullet}$. The reactions of $CF_3^{\bullet}$ with O_2 and O_3 yield species $CF_3O^{\bullet}$, $CF_3O_2^{\bullet}$ and $CF_3O_3^{\bullet}$ for which thermochemical estimates are given in Table 1. On the basis of these estimates, the important atmospheric catalytic cycles involving these species in the destruction of ozone are summarized below:

Cycle I

$$CF_3^{\bullet} + O_2 \rightarrow CF_3O_2^{\bullet} \qquad \Delta H = -37 \text{ Kcal/mol} \quad (1)$$

$$CF_3O_2^{\bullet} + O_3 \rightarrow CF_3O^{\bullet} + 2O_2 \qquad \Delta H = -41 \text{ Kcal/mol} \quad (2)$$

$$CF_3^{\bullet} + O_2 + O_3 \rightarrow CF_3O^{\bullet} + 2O_2$$

Cycle II

$$CF_3^{\bullet} + O_3 \rightarrow CF_3O_3^{\bullet} \qquad \Delta H = -58 \text{ Kcal/mol} \quad (3)$$

$$CF_3O_3^{\bullet} \rightarrow CF_3O^{\bullet} + O_2 \qquad \Delta H = -20 \text{ Kcal/mol} \quad (4)$$

$$CF_3^{\bullet} + O_3 \rightarrow CF_3O^{\bullet} + O_2$$

However, catalytic destruction of ozone would be possible only if O-atom abstraction (5) is faster than the more exothermic $F^{\bullet}$ atom abstraction (6).

$$CF_3O^{\bullet} + O \rightarrow CF_3^{\bullet} + O_2 \qquad \Delta H = -15 \text{ Kcal/mol} \quad (5)$$

$$\rightarrow CF_2O + FO^{\bullet} \qquad \Delta H = -45 \text{ Kcal/mol} \quad (6)$$

Furthermore, the intermediate trifluoromethoxy radical is also a source of fluorine atoms (via reaction 7) which are involved in the catalytic ozone destruction:

$$CF_3O^{\bullet} \rightarrow CF_2O + F \qquad \Delta H = +23 \text{ Kcal/mol} \quad (7)$$

From these thermochemical considerations, it is apparent that $CF_3O^{\bullet}$ may be important in CF_3X oxidation.

There have been several experimental attempts to detect $CF_3O^{\bullet}$. Christe and Pilipovich [2] attempted to isolate $CF_3O^{\bullet}$ by trapping the products of a low-pressure pyrolysis of CF_3OOCF_3 in argon at 8 K, but found no evidence for the radical in the matrix. Chen and Kochi [3] studied the photolysis of CF_3OOCF_3 by electron spin resonance spectroscopy, but $CF_3O^{\bullet}$ could not be detected directly. Rossi et al. [4] studied the reaction of $CF_3^{\bullet}$ radicals with ozone, but again the $CF_3O^{\bullet}$ radical was not observed. Infrared multiphoton decomposition of CF_3OOCF_3 yields trifluoromethoxy radicals [5,6], but as yet these have eluded direct experimental observation. Consequently ab initio quantum-chemical methods have been used to predict the structure and

vibrational spectrum of this radical [7].

Ab initio calculations were performed using the Cambridge analytic derivative package (CADPAC) at the 3-21G level of open-shell theory. The optimized geometries for the low lying excited states of $CF_3O^\bullet$ are given in Table 2. The ground electronic state in C_{3v} is degenerate (^2E) and undergoes Jahn-Teller distortion. Geometry optimization in C_s symmetry yields stationary points for the $^2A'$ and $^2A''$ states, stabilized by 0.33 and 0.28 Kcal mol^{-1} respectively, relative to the C_{3v} symmetrical structure. Analytical determination of the second derivatives reveals that the $^2A'$ structure is at a true minimum, but the $^2A''$ structure is at a saddle point on the potential energy hypersurface. Furthermore, the $^2A'$ and $^2A''$ structures are connected by pseudo-rotational procession about C_3 axis of the ^2E structure. The $^2A'$ first excited state of C_{3v} symmetry is calculated to be 30937 cm^{-1} above the ground ^2E state at the RHF/3-21G level.

Vibrational frequencies and relative intensities for the $^2A'$ state are presented in Table 3. These results, along with predicted vibrational frequencies for difluorodioxane [8], now allow us to comment upon the previously published work concerning the formation of CF_3O from the low-pressure pyrolysis of bis-(trifluoromethyl) peroxide, CF_3OOCF_3 [2]. Two sets of infrared absorption bands were reported in Ref. 2. One set of bands was still present at 42 K in a controlled-diffusion experiment; these were reported at 1897, 899, 824, 389 and 336 cm^{-1}. Bands at 1592, 1025, 986, 319 and 268 cm^{-1} had disappeared and there was uncertainty as to whether bands at 1271, 1076 and 659 cm^{-1} had also disappeared. It was concluded that at least two different species were involved. The possibility that some of the

unassigned infrared absorptions observed by Christe and Pilipovich [2], following low-pressure pyrolysis of CF_3OOCF_3, might be due to trifluoromethoxy radicals may be discounted on the grounds that those frequencies bear no relation to those calculated for CF_3O. Some of the bands which disappeared at 42 K show a resemblance to those predicted for difluorodioxane, and thus suggest that these bands may be due to difluorodioxane, but the evidence is inconclusive. Nevertheless, one species which might account for the absorptions still present at 42 K is trifluoromethyl fluoroformate, which has strong absorptions at 1901 cm^{-1} [10]: this compound could be formed according to

$$CF_3O^{\bullet} + CF_2O \rightarrow CF_3OCFO + F^{\bullet} \qquad [8]$$

Chen and Kochi [3] studied the photolysis of CF_3OOCF_3 and though unable to detect $CF_3O^{\bullet}$ directly using ESR, found evidence for the presence of adducts of CF_3O with alkenes, as in the reaction

$$CF_3O^{\bullet} + CH_2{=}CH_2 \rightarrow CF_3OCH_2CH_2^{\bullet} \qquad [9]$$

These results lend support to the proposed reaction (8) and to the suggestion that $CF_3O^{\bullet}$ is highly reactive.

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Table 1

Heats of formation (Kcal/mole) for $CF_3^{\bullet}$ and $CF_3O_x^{\bullet}$ radicals

Species	$\Delta H^{\circ}_{f,298}$
$CF_3^{\bullet}$	-112.4 ± 1.0
$CF_3O^{\bullet}$	-156.7 ± 2.3
$CF_3O_2^{\bullet}$	-149.9 ± 2.2
$CF_3O_3^{\bullet}$	-136.6 ± 3.0

Table 2

RHF/3-21G optimized geometries and energies for states of the trifluoromethoxy radical

	$CF_3O^{\bullet}$			
Coordinate	^2E (C_{3v})	$^2A'$ (C_s)	$^2A''$ (C_s)	$^2A_1$ (C_{3v})
CO (Angstroms)	1.385	1.383	1.383	1.442
CF'	1.332	1.332	1.333	1.316
CF	1.332	1.332	1.332	1.316
∢ (OCF)' (degrees)	109.9	107.1	112.2	108.5
∢ (OCF)	109.9	111.3	108.7	108.5
∢ (FCF)'	109.1	109.5	108.6	110.5
∢ (FCF)	109.1	108.2	110.0	110.5

Table 3

Calculated vibrational frequencies and relative intensities for the $^2A'$ ground state of $CF_3O^{\bullet}$

symmetry	mode	description	Frequency (cm^{-1}) unscaled	Frequency (cm^{-1}) scaled[a]	relative intensity
a'	1	CF str., asym.	1444	1256	0.97
	2	CO str.	1397	1251	0.77
	3	CF str., sym.	932	855	0.03
	4	CF_2 wag	641	611	0.08
	5	CF_2 scissor	608	578	0.10
	6	OCF^{-} def.	436	399	0.10
a"	7	CF str.	1470	1272	1.00
	8	CF_2 rock	636	584	0.02
	9	CF_2 twist	412	202	0.00

[a] Valence force constants scaled by factors determined for CF_2O and CF_3O^- (CO stretch 0.85, CF stretch 0.79, all bends 0.84); see reference [8].

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